(1) #US 4044358
Excellent SHAPE MEMORY OF "Mylar"
(2) HAS polyester

US-PAT-NO: **5747553**

DOCUMENT-IDENTIFIER: US 5747553 A

TITLE: Low pressure acrylic molding composition with fiber reinforcement

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Long fibrous fillers, such as glass, carbon, aramid, etc., are known to greatly
enhance strength, stiffness and toughness of plastic materials. Long fibers
being defined as lengths equal to or exceeding the critical aspect ratio of the
fiber matrix combination. Plastics reinforced with such long fibrous
inclusions, i.e., composites, exhibit physical and chemical properties that are
a composite of the properties of the fibrous fillers and plastic matrix.
Typically, the included fiber has tensile strength much higher than the resin
matrix, is insoluble in the resin matrix and is chemically, or physically
bonded to the resin matrix in such a way as to deflect a crack propagating
through the resin matrix along the length of the fiber-matrix interface.
Fibers turn the crack, absorb the energy of fracture, reduce the incidence of
through-and-through-fracture, and give composites their characteristic
properties of high strength, high stiffness, toughness and light weight. The
properties of some conventional **polymeric** materials and composites are
disclosed in CRC Practical Handbook of Materials Science, Ed. Charles T.
Lynch, 1994, pp. 547-548 (vinyls, ASA resins), 327-328 (glass fiber, organic
fiber) and 342 (organic matrix composites). While the use of long fibrous
fillers can provide advantageous physical properties, fiber

is difficult to incorporate into a resin matrix, particularly where the matrix resin is highly viscous.

The reinforcing fibers can comprise such materials as glass, metals, carbon, rayon, cellulose acetate, cellulose triacetate and the like, Mylar.TM. polyester, aramid/Kevlar.RTM., Nomex.RTM. aramid fiber or polyethylene fiber in continuous or discontinuous form. A preferred fiber is silanized chopped glass fiber. The preferred length of fiber reinforcement utilized with the acrylic-based doughs such as bulk molding compounds (BMC), particularly Elvacite.RTM. 2051 bulk molding compounds, falls in the range of 0.25 to 6.5 mm. The length of fiber reinforcement utilized with vinyl ester BIS-GMA doughs preferably ranges from 0.1 to 6.5 mm. Fibers can be used in an amount of from 10 wt. % up to about 90 wt. % for sheet materials. In dough molding compositions such as BMC, levels of fiber reinforcement above 25 wt. % show little advantage, although higher levels such as 50 wt % can be easily used. The dough molding compositions (BMC) preferably have at least 10 wt. % long fiber. Sheet molding compounds (SMC) can use discontinuous or continuous reinforcing fibers, filaments, **braided,** knit or woven fabrics.

Compositions of this invention can be prepared using conventional mixing equipment such as a high shear blender. The components of the molding composition are preferably first combined into two separate portions, a liquid mixture portion and solid mixture portion. The liquid mixture includes the liquid monomer acrylic resin, oligomer or polymer (vinylester resin, or polyester resin) optionally surfactant and catalyst. The dry ingredients are

mixed thoroughly in a high shear blender and typically include the solid acrylic polymer as filler, colorants, dispersing agents. Preferably, the reinforcing fibers are not blended into the solid mixture. Following preparation of the solid and liquid mixture portions, the two portions are combined in a low shear mixer for about five minutes, following which the reinforcing fibers are slowly added over an extended period. The fiber reinforcement is mixed so that there is no agglomeration of fibers and a uniform distribution is obtained by wetting these fibers. Once the fibers have been distributed throughout the liquid component, the mixture is allowed to stand (mature) for about two to five days with occasional stirring. This technique provides a bulk molding compound (BMC) consistent with the present invention. In forming sheet molding compounds (SMC), a mixture of liquid and solid components or a single component formulation are applied to a continuous fiber network of either knit, woven or **braided** fabrics or loose-lay filaments.

US-PAT-NO: 4448195

DOCUMENT-IDENTIFIER: US 4448195 A

TITLE: Reinforced **balloon** catheter

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Reinforced **balloon** catheter

A **balloon** catheter is formed by blow molding an elongated **polyurethane** tube so that one section of the tube has a thinned cross sectional **balloon** area between the distal end of tube which is sealed and its open proximal end. The **balloon** portion which is positioned adjacent the distal end has a thinner cross sectional area which allows a **balloon** to be formed if a fluid is introduced into the catheter by a syringe apparatus which is adapted to be attached to the lumen by a connection adaptor. A wire guide member is adapted to be inserted through the lumen for stretching the catheter when it is inserted into a blood vessel to stiffen the catheter and position it in a proper position. The wire guide member may also be mitred at predetermined intervals to determine the position of the catheter within the blood vessel.

Blood vessels and other tubular structures often undergo narrowing and obstruction. These vessels and tubular structures can be restored to their original diameter with some means of dilation. Various types of **balloon** catheters have been used for such dilating processes and are disclosed by many articles and patent references. U.S. Pat. No. 3,896,815 discloses a multisectional sealed **balloon** catheter with a guide wire

which is radio opaque.
The catheter **balloon** can be formed by expanding a distal tube portion of the
catheter during the manufacturing process. The prestretching operation renders
this portion of the catheter less resistant to expansion than is the unextended
remainder of the catheter.

U.S. Pat. No. 4,177,815 discloses an open ended urinary **balloon** catheter for
drainage in which a **balloon** is attached to a reduced diameter portion of the
catheter. The narrow portion of the catheter plus the thickness of the **balloon**
surface is not greater than the normal diameter of the catheter so that the
uninflated **balloon** does not present a special obstacle to the insertion of the
catheter through close fitting passages.

U.S. Pat. No. 3,978,863 discloses a **balloon**-tipped catheter with a radio
opaque position indicator means. A guide wire with enlarged end beads forms
the radio opaque position indicator. Thus, the position of the catheter may be
determined by X-ray techniques before the wire is removed and the **balloon** is
inflated.

In addition, the following U.S. Pat. Nos. 4,140,119; 4,149,539; and
4,188,954 generally relate to **balloon**-type catheters which are of interest.

The present invention pertains to **balloon** catheters and more specifically
relates to a one piece sealed **polyurethane** catheter with an inflatable **balloon**
tip. This **balloon** tip may be inflated when placed within the occlusion of an
artery or vein to dilate the vessel to form a clear path therethrough. The
catheter and **balloon** are a one piece unit with the **balloon** being a thin
catheter wall portion of exact shape and size. The

catheter may be formed by
blow molding tubing with a **fibrous reinforcement** of woven glass or fine fibers
of other materials. The woven fiber structure is placed over a **polyurethane**
extruded plastic tubing which is heated and the blown outward into a mold. The
molded **polyurethane** is then fused with the reinforcement fiber during this
procedure. Alternately the **balloon** can be formed by stretching a section of
the **polyurethane** tubing along the longitudinal axis of the tubing while it is
in a molten state.

A guide wire is placed within the catheter to stiffen the tubing and provide
guidance to the occlusion site. The guide wire stretches the **balloon** section
lengthwise in order to reduce the diameter of the **balloon** section so that it
can be introduced through an area of obstruction. The wire can be X-ray opaque
and can be mitred by notching the wire at set intervals to measure distances on
X-ray images. The catheter can be marked with opaque material or inflated with
such material so that its location within the body can be ascertained through
X-ray techniques. The tubing can also be banded with a steel collar at the
beginning and end of the thinned section to indicate the parameters of the
**balloon**.

In an alternative embodiment, **braided** shell wire reinforcement rather than the
aforementioned glass fiber is used, with the **braids** being placed at the
beginning and endings of the thinned portion but not at its center. This is to
reinforce the tubing onto the thinned portion.

FIG. 1 is an exploded view partially in cross-section of the inventive **balloon**
catheter apparatus inserted into a blood vessel before expansion of the **balloon**

portion of the catheter;

FIG. 2 is a exploded cross-sectional view of the inventive apparatus as shown in FIG. 1 with a syringe attached and fluid inserted into the **balloon** portion of the catheter;

FIG. 3 is a cross-sectional view of the inflated **balloon** catheter portion shown in FIG. 2;

FIG. 4 is a side view of a guide wire member which is used in the **balloon** catheter during insertion;

FIG. 5 is an enlarged cross-sectional view of the **balloon** catheter with wire outer **braids** along the tubing sections adjacent the **balloon** portion of the catheter; and

FIG. 6 is an enlarged cross-sectional view of the **balloon** catheter with fibers reinforcement fused in the walls of the catheter tubing.

The best mode and preferred embodiment of the invention is disclosed by FIGS. 1 through 4 and 6 and illustrates a catheter 10 made of **polyurethane** and formed with a blow molded thinned portion 12 in the wall of the catheter tubing 11. The portion 12 is thinned so that when a fluid 14 is introduced under pressure into the tubular catheter, a **balloon** 16 will form in the thinned portion 12. The tubular catheter 10 may be formed by sealing a distal end 15 of a **polyurethane** extruded tubing and placing the tubing within a mold lined with a reinforcement netting structure 110, preferably of woven glass fibers. The mold M partially shown in phantom in FIG. 5 includes a wider portion 50 adjacent the sealed distal portion 15 of the tube where the reinforcement lining structure is omitted. The tubing is heated and

blown outward to fuse with the reinforcement glass fiber structure, as well as to create a thinned out portion 12 of a size and position corresponding to that of the wider portion of the mold described above. The **balloon** portion thus is thinned with respect to the other portions of the tube and has an exact shape and size. Alternately, the **balloon** is formed in a thin section of the **polyurethane** tubing by stretching the **polyurethane** tubing in the long axis of the tubing while molten.

In use on a patient the thinned **balloon** portion 12 is stretched out by insertion of a wire guide 20 through lumen 19 so that the catheter 10 can be introduced through an area of obstruction 100 in the blood vessel 102. When the thinned portion 12 of the catheter 10 is within obstruction 100, the guide wire 20 is removed and a syringe 22 is attached to an adapter 24 on the proximal end 17 of the tube to inflate the **balloon**. A non-compressible medically compatible liquid 14 is generally used as the fluid for this purpose. The catheter 10 is placed in an open vessel 102 at surgery or can be introduced into an artery through a needle. The catheter can contain radio opaque markings so that it can be positioned in areas of narrowing by use of X-ray imaging. The **balloon** 16 can also be inflated with radio opaque material.

A guide wire 20 is longer than the catheter tubing and when placed in the catheter 10 locks into the adapter 24. This insures that the thinned portion 12 of the catheter 10 is stretched to proper length in the longitudinal direction during the catheter introduction. The guide wire 20 serves to stretch and stiffen the tubing and acts as a radio opaque guide wire. The

guide wire 20 can be mitred as shown by the numerals 27 to measure distances in
the X-ray image by notching the wire 20 at set intervals. The tubing can also
be banded with steel collars 32 as shown in FIG. 6 at the beginning and ending
of the thinned portion 12 to indicate the length of the **balloon**.

After the catheter 10 has been placed in a correct position in obstructed area
100, the guide wire 20 is removed; a syringe 22 is connected to adaptor 24 and
the **balloon** 16 is expanded with fluid.

In an alternate embodiment, shown in FIG. 5, **braided** shell wire reinforcement
is used rather than the preferred embodiment of woven glass or fine fibers and
the **braids** are placed at the beginning and end of the thinned portion of the
**balloon** section, but not at the center. This reinforces the tubing onto the
thinned portion 12, but not in the center of the thinned portion. In this
regard, La Place's law states that the tension on a wall is proportional to
both the pressure within the catheter 10 and the diameter thereof.

While the **balloon** 16 is without reinforcement, it is also constrained by the
occlusion 100 and will not expand to the point where the tensile strength of
the **balloon** 12 equals the tension thereon. Thus, **balloon** 12 will not rupture.

1. An expandable **balloon** catheter comprising an elongate flexible cylindrical
tube having proximal and distal ends, said tube defining an inflation lumen
means within said tube, said lumen means being sealed at said distal end and
open at said proximal end of said tube, said tube including a unitary **balloon**
portion adjacent to and spaced apart from said distal end, said **balloon** portion

of said tube being thinner than the remaining portion of said tube, and a woven reinforcing structure combined with said remaining portion of said tube, said woven reinforcing structure overlapping opposite ends of said **balloon** portion to reinforce the remaining portion of the tube onto the **balloon** portion.

2. The apparatus of claim 1, wherein said tube is formed from **polyurethane**.

5. The apparatus of claim 1, wherein said woven reinforcing structure is a **braided** wire.

6. The apparatus of claim 1, including **metal** banding surrounding said tube on opposite ends of said **balloon** portion of said tube to indicate the length of the **balloon** portion.

7. A unitary blow-molded expandable **balloon** catheter comprising an elongated hollow tube with an external diameter no greater than the internal diameter of a human blood vessel into which it is to be inserted, said tube provided with an inflation lumer, a sealed distal end for insertion into said human blood vessel, and an open proximal end for connection to inflation means and tensioning means, said tube defining an inflatable **balloon** comprising a unitary portion of said tube adjacent to and spaced apart from said distal end, said **balloon** being of predetermined length and of lesser tube wall thickness than that of said tube between said **balloon** and said proximal end and between said **balloon** and said distal end, and said elongated hollow tube between said **balloon** and said proximal end and between said **balloon** and said distal end being composed of an elastomeric **polymer** containing a woven **fibrous** **reinforcement** material to reinforce these portions of the

tube onto the **balloon**
portion.

US-PAT-NO: 3616199

DOCUMENT-IDENTIFIER: US 3616199 A

TITLE: REINFORCING PROCESS

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The addition of **fibrous polyester reinforcing** material to rubber stock can be improved by treating the fibrous material with a polysulfonyl azide having the formula

This invention relates to a process of improving the adhesion of **fibrous polyester reinforcing** material to rubber stock and to the products so produced. In particular, this invention relates to a process of improving the adhesion of polyester fiber, including yarn, fabric and cord to rubber stock by treatment of the fiber with a polysulfonyl azide and to the products so produced.

Now, in accordance with this invention it has been found that polyester fiber, including yarn, fabric, cord and the like, having good adhesion to vulcanized rubber stock can be prepared by modifying the fiber with a polysulfonyl azide as described hereinafter. The fiber-to-rubber adhesion can be further improved for some usages if an adhesive coating is applied to the modified fiber. The coating frequently used is a dispersion of a phenol-aldehyde condensation copolymer (i.e. resin) and a vinylpyridine containing rubber **polymer** latex. The modified polyester reinforcing material of this invention can be used in any type of rubber tire, including automobile, truck, tractor, and aircraft tires, as well as in rubber belting and rubber hose where

low elongation,
strength and dimensional stability are important.

The first step in the process of this invention is the modification of polyester fiber by treatment with a polysulfonyl azide. This is accomplished by contacting the fiber with the polysulfonyl azide compound as for example, by dipping, spraying, brushing, or running it over a coated roll with a dispersion or solution of the polysulfonylazide in a suitable liquid. Exemplary of suitable organic solvents for the polysulfonyl azides are methylene chloride, trichloroethylene, methyl ethyl ketone, benzene and toluene. Water can also be used, with the polysulfonyl azides being applied as an aqueous suspension, emulsion or dispersion. In the next step of the process, the thus treated fiber is heated to a temperature above the decomposition point of the sulfonyl azide groups resulting in surface modification of the fiber. This temperature will in general be from about 120.degree. C. to about 250.degree. C. Various amounts of the polysulfonyl azide treating agents can be used. The optimum amount will depend upon the amount of modification desired, and the specific polysulfonyl azide compound used. In general, the amount added based on the fiber will be from about 0.1 to about 5.0 percent by weight. Next, the modified fibrous material may be coated with a standard industrial coating, or adhesive, which is compatible with the rubber in which the fibrous reinforcing material is to be embedded. As stated above, the coating is generally a mixture of a phenol aldehyde resin and a vinylpyridine **polymer** latex. In all cases the exact selection of the **polymer** latex components will be made to achieve compatibility with the rubber used in the final fiber-to-rubber composite. Preferably, the phenol-aldehyde resin will be

prepared from
resorcinol and formaldehyde, although other phenols such as hydroxybenzene,
para-cresol, and pyrogallol can also be used. The mole ratio of phenolic
compound to aldehyde in the phenol-aldehyde resin can be varied between about
1:1.02 to about 1:5. The phenol-aldehyde resin will generally be aged for a
period of from about 0.5 to about 6 hours before mixing with the vinylpyridine
**polymer** latex. The said aging can be carried out at room temperature or
elevated temperatures. For use with natural rubber and styrene-butadiene
rubber the vinylpyridine **polymer** latex will preferably be a terpolymer of a
vinylaryl monomer, a diene monomer, and a vinylpyridine monomer. The vinylaryl
monomer will preferably be styrene, although other monomers such as
vinyltoluene can be used. The diene monomers which can be used in preparing
the **polymer** latex are open chain conjugated diolefins, including for example,
1,3-butadiene, isoprene, 2,3 -dimethyl-1,3-butadiene,
1,2-diethyl-1,3-butadiene, and piperylene. The vinylpyridine monomers most
useful in preparing the **polymer** latex are alpha-vinylpyridine,
5-ethyl-2-vinylpyridine, and 2-methyl-5-vinylpyridine, although other monomers
such as 5-butyl-2-vinylpyridine, 5-heptyl-2-vinylpyridine,
6-methyl-2-vinylpyridine, 4,6-dimethyl-2-vinylpyridine, and
2-methyl-4-vinylpyridine can be used. The vinylpyridine content of the
terpolymer is usually from about 5 percent to about 25 percent, the vinylaryl
monomer content from about 5 percent to about 35 percent and the diene monomer
content from about 50 percent to about 85 percent. The rubber **polymer** latex
can be admixed with the phenol-aldehyde resin in ratios of between about 2:1
and about 10:1. Following the mixing of the two ingredients the pH will
generally be adjusted to about 9.5 to about 10.5 using an inorganic base such

as ammonium hydroxide.

The modified fibrous material can be coated with the conventional coating
uniformly by dipping, spraying, running the material over a coated roll, or
other conventional procedure. The coating will amount to from about 2 percent
to about 10 percent by weight of the material. The coated material will then
be cured for a short time such as from about 1 to about 10 minutes at a
temperature of between about 250.degree. F. and about 450.degree. F. The
cured coating is a hard **polymer** which is very adherent to the modified fibrous
material and produces excellent adhesion between the modified material and
conventionally vulcanized rubber. It may be desirable in certain cases, to
omit the latex coating, thereby directly embedding the modified polyester
fibrous material in a vulcanizable rubber stock and curing to obtain a
reinforced rubber product. Such products reinforced with modified polyester
fibrous material are superior to products reinforced with nonmodified polyester
fibrous material, but exhibit a proportionate decrease in adhesive strength
over those reinforced with modified fibrous material and coated with the
above-described coating composition.

1. In a process of adhering **fibrous polyester reinforcing** material to rubber
stock the improvement of first contacting said fibrous material with a
polysulfonyl azide having the formula

4. The process of claim 1 wherein the **fibrous polyester reinforcing** material
is poly(ethylene terephthalate) tire cord.

5. A **fibrous polyester reinforcing** material modified by reaction with a
polysulfonyl azide having the formula

6. A vulcanized rubber product reinforced with **fibrous polyester reinforcing**
material said material having been first modified by heating with a small
amount of a polysulfonyl azide having the formula